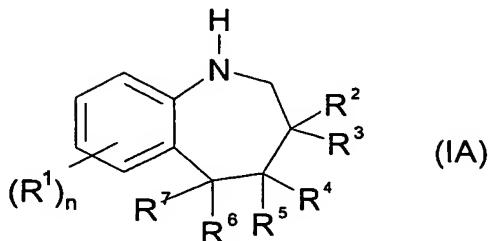


## CLAIMS

1. A method of preparing at least one benzazepine compound of general formula (IA):



in which:

R<sup>1</sup> represents a halogen atom chosen from chlorine, fluorine, bromine and iodine, an alkyl, haloalkyl, alkenyl, alkynyl, acyl, aryl, arylalkyl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle, a polymer chain, or a group -(CH<sub>2</sub>)<sub>m</sub>-OR<sup>k</sup>, -CH(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-S(O)R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>NR<sup>k</sup>R<sup>l</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>3</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NO<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>-CN, -(CH<sub>2</sub>)<sub>m</sub>-PO(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SiR<sup>k</sup>R<sup>l</sup>R<sup>m</sup>, -(CH<sub>2</sub>)<sub>m</sub>-COOR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NCOR<sup>k</sup>, or -(CH<sub>2</sub>)<sub>m</sub>-NR<sup>k</sup>R<sup>l</sup>, with:

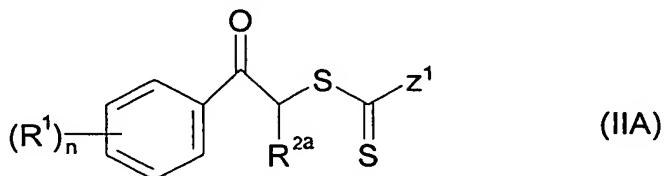
$R^k$ ,  $R^l$  and  $R^m$  each independently denoting a hydrogen atom, an alkyl, haloalkyl, acyl, aryl, alkenyl, arylalkenyl, alkynyl, arylalkynyl, aralkyl or alkaryl group, a hydrocarbon-based ring or a heterocycle, or else  $R^k$  and  $R^l$  form, together with the atom to which they are attached, a heterocycle.

with  $m$  denoting an integer greater than or equal to 0.

20 - n represents an integer chosen from 0, 1, 2, 3 and 4, with, when n is greater than or equal to 2, it being possible for the corresponding R<sup>1</sup> groups to be identical or different, and, where appropriate, to form, together, a hydrocarbon-based ring or a heterocycle,

25 - R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> represent, independently of one another, a hydrogen atom, a halogen atom chosen from chlorine, fluorine and bromine, an alkyl, haloalkyl, alkenyl, alkynyl, acyl, aryl, arylalkyl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle, a polymer chain, or a group -(CH<sub>2</sub>)<sub>m</sub>-OR<sup>k</sup>, -CH(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-S(O)R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>NR<sup>k</sup>R<sup>l</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>3</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NO<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>-CN,

-(CH<sub>2</sub>)<sub>m</sub>-PO(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SiR<sup>k</sup>R<sup>l</sup>R<sup>m</sup>, -(CH<sub>2</sub>)<sub>m</sub>-COOR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NCOR<sup>k</sup> or -(CH<sub>2</sub>)<sub>m</sub>-NR<sup>k</sup>R<sup>l</sup>, with R<sup>k</sup>, R<sup>l</sup>, R<sup>m</sup> and m as defined above,  
 or R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> form, in pairs, one or more hydrocarbon-based ring(s) or heterocycle(s), with at least one of the R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> groups representing a  
 5 hydrogen atom,  
 from at least one compound of general formula (IIA)



in which

- Z<sup>1</sup> represents a group chosen from:
  - 10 (i) alkyl, acyl, aryl, aralkyl, alkene or alkyne groups, and hydrocarbon-based rings or heterocycles,
  - (ii) an -OR<sup>a</sup> or -SR<sup>a</sup> group in which R<sup>a</sup> is a group chosen from:
    - an alkyl, haloalkyl, alkenyl, alkynyl, acyl, aryl, arylalkyl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle, or else a polymer chain;
    - a -CR<sup>b</sup>R<sup>c</sup>PO(OR<sup>d</sup>)(OR<sup>e</sup>) group in which:
      - R<sup>b</sup> and R<sup>c</sup> each represent, independently of one another, a hydrogen atom, a halogen atom, an alkyl or perfluoroalkyl group, a hydrocarbon-based ring or a heterocycle, or else an -NO<sub>2</sub>, -NCO or -CN group, or a group chosen from the groups of type -R<sup>f</sup>, -SO<sub>3</sub>R<sup>f</sup>, -OR<sup>f</sup>, -SR<sup>f</sup>, -NR<sup>f</sup>R<sup>g</sup>, -COOR<sup>f</sup>, -O<sub>2</sub>CR<sup>f</sup>, -CONR<sup>f</sup>R<sup>g</sup>, -NR<sup>f</sup>COR<sup>g</sup>, in which R<sup>f</sup> and R<sup>g</sup> each independently denote an alkyl, alkenyl, alkynyl, cycloalkenyl, cycloalkynyl or aryl group optionally condensed with a heterocycle, alkaryl, arylalkyl or heteroaryl,
      - 20 • or else R<sup>b</sup> and R<sup>c</sup> form, together with the carbon atom to which they are attached, a C=O or C=S group or else a hydrocarbon-based ring or a heterocycle; and
      - R<sup>d</sup> and R<sup>e</sup> each represent, independently of one another, a radical corresponding to one of the definitions given above for the R<sup>f</sup> group;
      - 25 • or else R<sup>d</sup> and R<sup>e</sup> form, together, a hydrocarbon-based chain containing from 2 to 4 carbon atoms, optionally interrupted with a group chosen

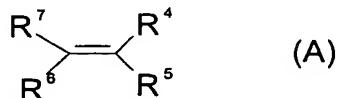
from  $-O-$ ,  $-S-$  and  $-NR^h-$ ; where  $R^h$  corresponds to one of the definitions given above for the  $R^f$  group;

(iii) an  $-NR^iR^j$  group, in which:

- $R^i$  and  $R^j$  represent, independently of one another, a radical chosen from an alkyl, haloalkyl, alkenyl, alkynyl, acyl, ester, aryl, arylalkyl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle; or
- $R^i$  and  $R^j$  form, together, a hydrocarbon-based chain containing from 2 to 4 carbon atoms, optionally interrupted with an  $-O-$ ,  $-S-$ , or  $-NR^h-$  group, where  $R^h$  corresponds to one of the definitions given above for the  $R^f$  group,
- $R^{2a}$  represents a group chosen from a hydrogen atom, a halogen atom, in particular fluorine, chlorine or bromine, an alkyl, haloalkyl, acyl, aryl or arylalkyl group, or else a hydrocarbon-based ring or a heterocycle, a polymer chain, or a group  $-(CH_2)_m-OR^k$ ,  $-CH(OR^k)(OR^l)$ ,  $-(CH_2)_m-SR^k$ ,  $-(CH_2)_m-S(O)R^k$ ,  $-(CH_2)_m-SO_2R^k$ ,  $-(CH_2)_m-SO_2NR^kR^l$ ,  $-(CH_2)_m-SO_3R^k$ ,  $-(CH_2)_m-NO_2$ ,  $-(CH_2)_m-CN$ ,  $-(CH_2)_m-PO(OR^k)(OR^l)$ ,  $(CH_2)_m-SiR^kR^lR^m$ ,  $-(CH_2)_m-COOR^k$ ,  $-(CH_2)_m-NCOR^k$  or  $-(CH_2)_m-NR^kR^l$ , in which  $R^k$ ,  $R^l$ ,  $R^m$  and  $m$  are as defined above, and preferably a hydrogen atom,
- $R^1$  and  $n$  are as defined above,

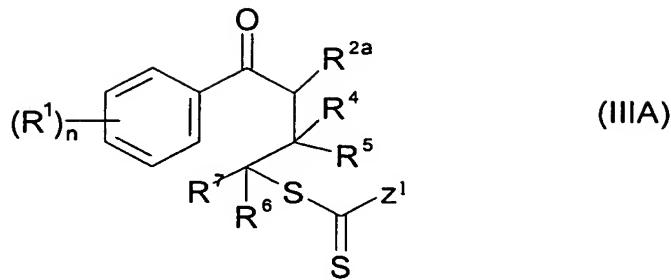
comprising at least the stages consisting in:

- a- reacting said compound of general formula (IIA) with at least one olefin of general formula (A)



in which:

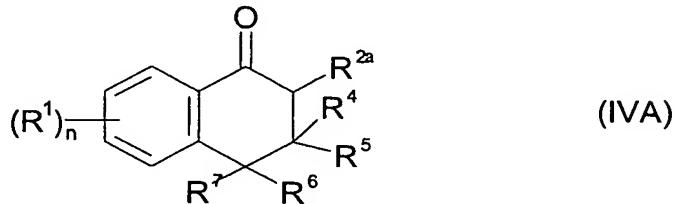
$R^4$ ,  $R^5$ ,  $R^6$  and  $R^7$  are as defined above, with at least one of the  $R^4$ ,  $R^5$ ,  $R^6$  or  $R^7$  groups representing a hydrogen atom,  
so as to obtain at least one compound of general formula (IIIA)



in which:

$R^1, R^{2a}, R^4, R^5, R^6, R^7, Z^1$  and  $n$  are as defined above,

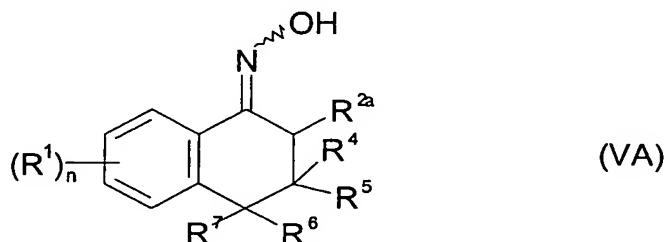
5 b- cyclizing, by radical-based process, said compound of general formula (III A) so as to obtain at least one tetralone compound of general formula (IV A)



in which:

10  $R^1, R^{2a}, R^4, R^5, R^6, R^7$  and  $n$  are as defined above,

c- converting said compound of general formula (IV A) into at least its oxime derivative of general formula (V A)



15 in which:

$R^1, R^{2a}, R^4, R^5, R^6, R^7$  and  $n$  are as defined above,

20 d- converting said compound of general formula (V A), by Beckmann rearrangement and consecutive reduction(s), into at least one compound of general formula (I A), and

e- recovering said compound of general formula (I A).

2. The method as claimed in claim 1, characterized in that said benzazepine compound corresponds to general formula (IA) in which  $n = 1$ .

3. The method as claimed in claim 2, characterized in that the  $R^1$  group is in the para-position.

5 4. The method as claimed in any one of claims 1 to 3, characterized in that the benzazepine compound corresponds to general formula (IA) in which  $R^1$  represents a halogen atom or an alkoxy group.

5 10 5. The method as claimed in any one of claims 1 to 4, in which said benzazepine compound corresponds to general formula (IA) in which  $R^2$  and  $R^3$  each independently represent a hydrogen atom or an alkyl group.

6. The method as claimed in any one of claims 1 to 4, in which said benzazepine compound corresponds to formula (IA) in which  $R^2$  and  $R^3$  each represent a halogen atom, and in particular a chlorine, fluorine or bromine atom.

15 7. The method as claimed in any one of claims 1 to 6, characterized in that, in the compound of formula (IIA),  $Z^1$  represents  $-OR^a$ , and in particular  $R^a$  represents a  $C_1$  to  $C_{12}$  alkyl group.

8. The method as claimed in any one of claims 1 to 7, characterized in that the olefin of general formula (A) is disubstituted, and in particular terminal disubstituted or cyclic.

20 9. The method as claimed in any one of claims 1 to 7, characterized in that the olefin of general formula (A) is monosubstituted, and in particular  $R^4$ ,  $R^5$  and  $R^6$  each represent a hydrogen atom.

25 10. The method as claimed in any one of claims 1 to 9, characterized in that the substituent(s) of said olefin of general formula (A) is (are) chosen from -Oacyl groups and groups of  $-(CH_2)_pCN$  type with  $p$  representing an integer ranging from 1 to 10.

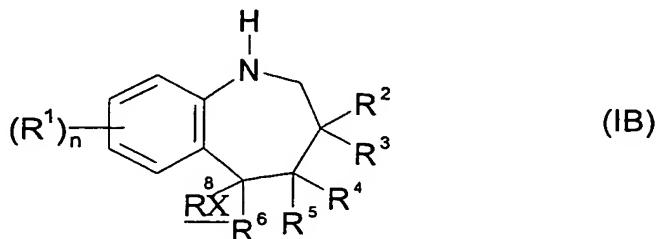
11. The method as claimed in any one of claims 1 to 10, characterized in that the olefin of formula (A) is chosen from:

- vinyl pivalate,
- allyl cyanide, and
- N-vinylphthalimide.

30 12. The method as claimed in any one of claims 1 to 11, characterized in that stage a is carried out in the presence of an effective amount of at least one radical initiator, in particular dilauroyl peroxide (DLP).

13. The method as claimed in any one of claims 1 to 12, characterized in that stage b is carried out in an acidic medium, in particular in the presence of camphorsulfonic acid.

14. A method of preparing at least one compound of general formula 5 (IB)



in which:

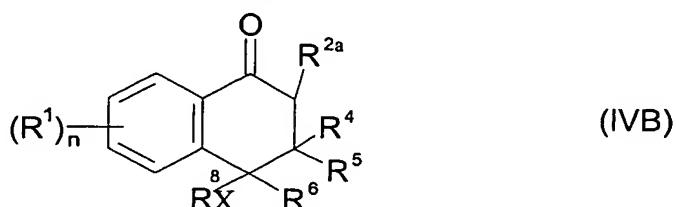
$R^1, R^2, R^3, R^4, R^5, R^6$  and  $n$  are as defined in claims 1 to 6,

$X$  represents  $O$ ,  $NR^9$ ,  $S$ ,  $S(O)$ ,  $SO_2$ ,  $SO_2NR^9$ , and  $R^8$  and  $R^9$  represent,

10 independently of one another, a hydrogen atom, an alkyl, haloalkyl, alkenyl, alkynyl, acyl, aryl, arylalkyl, alkaryl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle, or a polymer chain, where appropriate substituted,

or else  $R^8$  and  $R^9$  form, together with the atom to which they are attached, a

15 heterocycle from at least one compound of general formula (IVB)



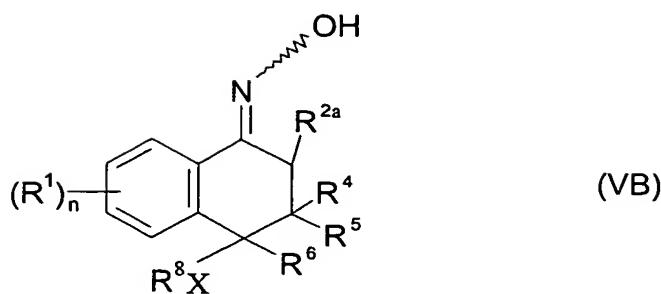
in which:

$R^1, R^4, R^5, R^6, R^8, X$  and  $n$  are as defined above, and

$R^{2a}$  is as defined in claim 1,

20 comprising at least the stages consisting in:

a'- converting said compound of general formula (IVB) into at least its oxime derivative of general formula (VB)



in which:

R<sup>1</sup>, R<sup>2a</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>8</sup>, X and n are as defined above,

5        b'- converting said compound of general formula (VB), by Beckmann rearrangement and consecutive reduction(s), into at least said compound of general formula (IB), and

      c'- recovering said compound of general formula (IB).

15. The method as claimed in any one of claims 1 to 14, characterized in that the stage consisting of preparation of the oxime derivative of formula (VA) or (VB) comprises placing said compound of general formula (IVA) or (IVB) in the presence of an effective amount of nitromethane or of hydroxylamine.

16. The method as claimed in claim 15, characterized in that it also comprises a stage consisting of recovery of the product of formula (VA) or (VB), in particular by recrystallization.

15        17. The method as claimed in any one of claims 1 to 16, characterized in that the conversion of the compounds (VA) or (VB) by Beckmann rearrangement is carried out in the presence of an effective amount of PCl<sub>5</sub>.

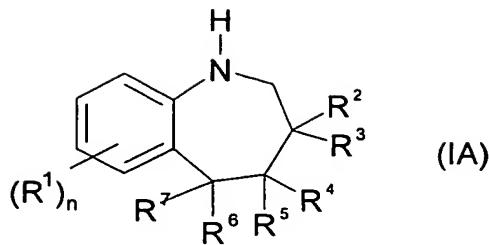
18. The method as claimed in claim 17, characterized in that the PCl<sub>5</sub> is used in molar excess relative to the compounds of formula (VA) or (VB).

20        19. The method as claimed in any one of claims 1 to 18, characterized in that the product derived from the Beckmann rearrangement is reduced with an effective amount of at least one metal reducing agent, in particular zinc.

25        20. The method as claimed in claim 19, characterized in that the reduction product obtained is treated with an effective amount of reducing agent, especially of BH<sub>3</sub>, and in particular of BH<sub>3</sub>·THF.

21. The method as claimed in any one of claims 1 to 18, characterized in that the product derived from the Beckmann rearrangement is treated with an effective amount of NaBH<sub>4</sub>.

22. A compound of general formula (IA)



in which:

R<sup>1</sup> represents a halogen atom chosen from chlorine, fluorine, bromine and iodine, an alkyl, alkenyl, alkynyl, acyl, aryl, arylalkyl, arylalkenyl or arylalkynyl group, or else a hydrocarbon-based ring or a heterocycle, a polymer chain, or a group -(CH<sub>2</sub>)<sub>m</sub>-OR<sup>k</sup>, -CH(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-S(O)R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>2</sub>NR<sup>k</sup>R<sup>l</sup>, -(CH<sub>2</sub>)<sub>m</sub>-SO<sub>3</sub>R<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NO<sub>2</sub>, -(CH<sub>2</sub>)<sub>m</sub>-CN, -(CH<sub>2</sub>)<sub>m</sub>-PO(OR<sup>k</sup>)(OR<sup>l</sup>), -(CH<sub>2</sub>)<sub>m</sub>-SiR<sup>k</sup>R<sup>l</sup>R<sup>m</sup>, -(CH<sub>2</sub>)<sub>m</sub>-COOR<sup>k</sup>, -(CH<sub>2</sub>)<sub>m</sub>-NCOR<sup>k</sup> or -(CH<sub>2</sub>)<sub>m</sub>-NR<sup>k</sup>R<sup>l</sup>, with R<sup>k</sup>, R<sup>l</sup> and R<sup>m</sup> and m as defined in claim 1,

R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are as defined in claims 1 to 6,

R<sup>7</sup> = -XR<sup>8</sup>, XR<sup>8</sup> being as defined in claim 14,

n = 1.

23. A compound as claimed in claim 22, characterized in that it is chosen from:

15 - 7-chloro-2,3,4,5-tetrahydro-1H-benzo[b]azepin-5-yl 2,2-dimethylpropionate,

- 7-fluoro-2,3,4,5-tetrahydro-1H-benzo[b]azepin-5-yl 2,2-dimethylpropionate,

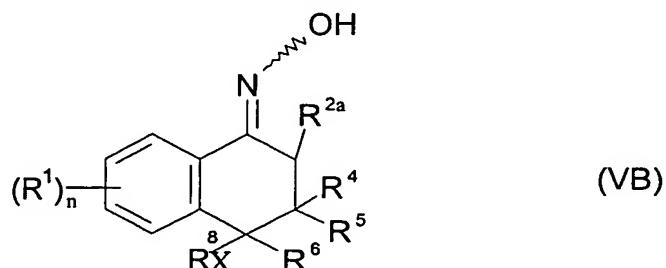
- 7-methoxy-2,3,4,5-tetrahydro-1H-benzoazepin-5-yl 2,2-dimethylpropionate,

- (7-fluoro-2,3,4,5-tetrahydro-1H-benzo[b]azepin-5-yl)acetonitrile,

- 3,3,7-trichloro-2,3,4,5-tetrahydro-1H-benzo[b]azepin-5-yl 2,2-dimethylpropionate, and

- derivatives thereof.

24. A compound of general formula (VB)



in which:

$R^1$ ,  $R^{2a}$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as defined in claims 1 to 6,  $XR^8$  is as defined in claim 14 and  $n = 1$ .

25. A compound as claimed in claim 24, characterized in that it is chosen from:

5 - 4-[(E)-hydroxyimino]-7-chloro-1,2,3,4-tetrahydronaphthalen-1-yl 2,2-dimethylpropionate,

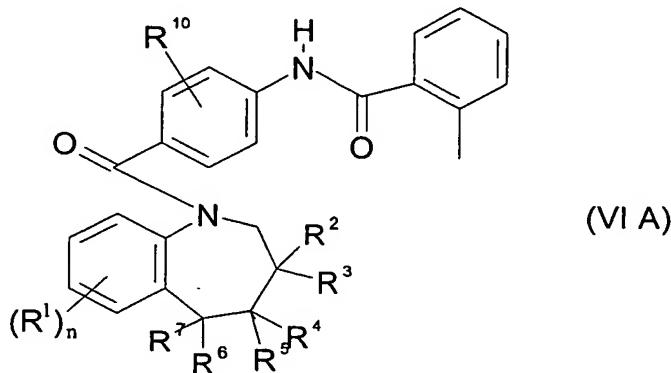
- 4-[(E)-hydroxyimino]-7-fluoro-1,2,3,4-tetrahydronaphthalen-1-yl 2,2-dimethylpropionate, and

- 4-[(E)-hydroxyimino]-7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl

10 2,2-dimethylpropionate, and

- derivatives thereof.

26. A method of preparing a benzazepine of general formula (VIA):



in which:

15  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $n$  are as defined in claim 22, and

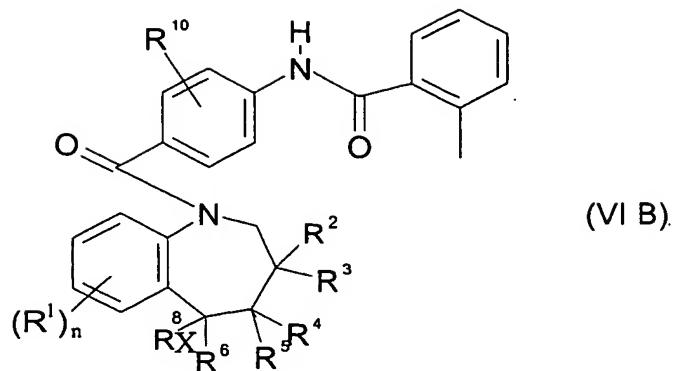
$R^{10}$  represents a hydrogen atom or an alkyl or acyl group, and in particular a methyl group,

comprising at least the conversion of a compound of general formula (IIA) into a

compound of formula (IA) according to the method as claimed in any one of

20 claims 1 to 21.

27. A method of preparing a benzazepine of general formula (VIB):



in which:

$R^1, R^2, R^3, R^4, R^5, R^6, XR^8$  and  $n$  are as defined in claim 22, and

5  $R^{10}$  represents a hydrogen atom or an alkyl or acyl group, and in particular a methyl group,  
comprising at least the conversion of a compound of general formula (IVB) into a compound of formula (IB) according to the method as claimed in any one of claims 14 to 21.